

Porphyrin-Fullerene Interaction in Solution and Solid: Dynamics of the Electron Transfer

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Electron transfer (ET) interaction of porphyrin and fullerene has been studied recently in great details [1-4]. Already the first experiments have shown that a complete charge separation (CCS) can be achieved for covalently linked porphyrin-fullerene dyad, as was indicated by the time resolved absorption spectroscopy [1]. However, further investigations of the PC dyads revealed new characters of the ET interaction. An exciplex-like intermediate state was observed for phytychlorin-fullerene dyads [2]. The formation of the exciplex can be observed in the emission of the dyad in the near IR region. The photo-dynamics studies of the dyad suggest that the exciplex is the precursor of the CCS state.

The near IR emission was observed for rather different types porphyrin-fullerene complexes. As an example Fig. 1 presents the emission of the covalently linked dyad in benzene [4] and of solid film made of mixture of Zn porphyrin (ZnDPP) and fullerene (C₆₀). In both cases one can note a close proximity of the chromophores and, as a result, relatively high coupling of the electron orbitals of the donor and acceptor ($V \sim 200 \text{ cm}^{-1}$). The emission can be analyzed in frame of Marcus ET theory and reveals fundamental energetic parameters of the porphyrin-fullerene ET interaction [3,4].

The close contact of porphyrin and fullerene seems to be a necessary condition for an appearance of the near IR emission band. For dyads characterized by relatively big separation of donor and acceptor (edge-to-edge distance $> 4 \text{ \AA}$) the emission was not observed. Nevertheless, in some cases of the "long distance" dyads, thorough analysis of the photo-dynamics allows one to suggest a formation of an intermediate state between the locally excited and CCS states. This can be illustrated by the example of ZnP-S1-C₆₀ dyad (edge-to-edge distance is $\sim 6 \text{ \AA}$) in benzonitrile (Fig. 2). The emission at 620 nm (porphyrin singlet excited state) decays with lifetime of 2 ps. The CCS state is, however, formed with the time constant of 12 ps (transient absorption data at 620 and 1050 nm). The state of the dyad between 2 and 12 ps is characterized by strong bleaching of the porphyrin ground state absorption bands and cannot be attributed to a locally excited fullerene (as the result of energy transfer). This indicates a presence of a new intermediate state, which eventually involves both chromophores and is considered as a precursor of the CCS state.

Based on the results presented above can proposed to model the formation of the CCS state (Fig. 3). Additional new experimental data will be presented to

confirm the model. The discussion of the model is based on estimations of principal energetic parameters of the ET reactions obtained for different systems.

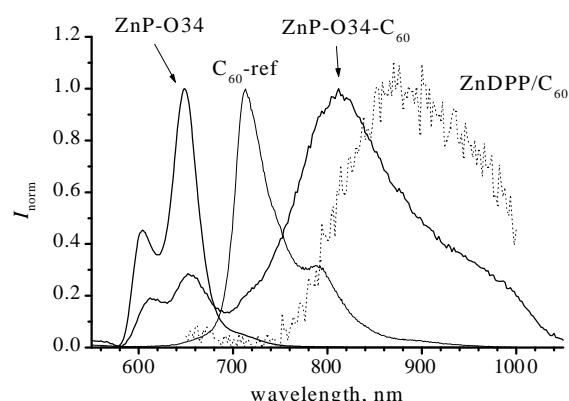


Fig. 1. Emission spectra of ZnP-O34-C₆₀, ZnP-O34 and C₆₀-ref in benzene and of ZnDPP/C₆₀ = 1:1 mixed film.

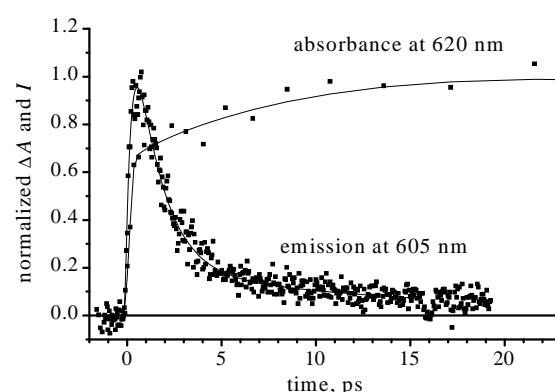


Fig. 2. Decay of emission at 605 nm ($\tau = 2 \text{ ps}$) and formation of transient absorption at 620 nm ($\tau = 12 \text{ ps}$) for ZnP-S1-C₆₀ dyad in benzonitrile.

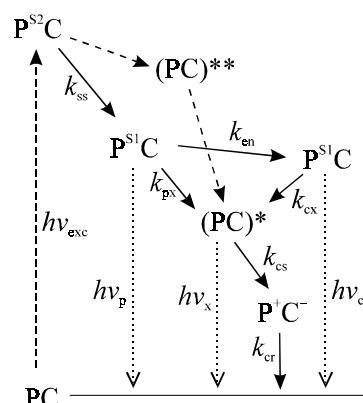


Fig. 3. Kinetic scheme of formation of complete CS state.

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